This section documents attempts to quantify the amount of PCB lost during the remediation project, and to relate that to the quantity removed during the project. It should be noted that calculations and models of this type are complex and require simplifying assumptions to be usable at all. One of the major difficulties encountered with PCBs is the fact that there are multiple pathways available for the material to become airborne.

PCBs can exist in a variety of states, with transitions between the different states governed by complex and incompletely understood thermodynamic mechanisms. While in the sediment, the PCBs are most probably bound with the organic matter within the sediments. Although they are not very water soluble, there is an equilibrium partitioning between the sediment and the water, leading to increased concentrations in the water passing over the contaminated sediments.

Likewise, while PCBs are not especially volatile, there is an equilibrium between the air and the water, or, in the case of exposed sediments, between the sediments and air, governed by a variety of factors including water and air temperature and other meteorological conditions, as well as the relative concentrations between the air and water. A number of experimentally determined equilibrium constants have been derived to help describe the conditions under which the PCBs will move from water or sediments to air or vice versa. In addition to the direct volatilization pathway, sediment bound PCBs may be suspended in air by wind action, thereby increasing atmospheric concentrations in a manner less subject to thermodynamic extrapolation.

Within the context of the remediation project, there are numerous potential sources for PCB to the atmosphere. First, there is the river itself, and the potential that local water concentrations would increase as a result of the dredging, thereby increasing the thermodynamic pressure for volatilization. This potential has been ignored in the course of this project, as there was not sufficient background data collected to be able to differentiate between the river at rest and during dredging.

Potential sources directly related to the remediation project include volatilization from the settling basins and water treatment system, volatilization from the filter presses and sediment dewatering processes, and suspension of particulate bound PCBs from the dewatered sediment stockpile and during truck loading. The magnitude of each of these sources is unknown, and attempts to quantify or model emissions from them require significant assumptions.

In the following sections, emissions are estimated in several different ways. The first approach uses an equation derived from EPA guidance on estimating emissions from superfund sites. This equation attempts to relate the increase in concentration between upwind and downwind sites to emissions as a function of distance and assumed dispersion conditions. This approach treats the remediation area as a single area source. The next approach involves application of a standard source model in two different ways, first treating the remediation project as a single large point source, and then attempting to differentiate between the different potential sources.

#### **Emission Calculations**

The design of the monitoring project allows for the application of the upwind/downwind screening technique to estimate emissions. The concentric ring deployment and total number of samplers ensured that no matter which way the wind was blowing there would be sampling locations both upwind and downwind of the remediation site.

The general theory behind this calculation method is that the emission rate across an area will be directly related to the difference between upwind and downwind concentrations, and the transit time across the source. The transit time in turn is related to the wind speed, distance to the sampling site, and dispersion parameters based on the ambient conditions at the time. A variety of different standard dispersion factors are available. The parameters used in this report are Briggs Urban Dispersion Parameters, which attempt to account for the generic urban landscape's affect on dispersion.

The following equation is used to estimate emissions in this fashion:

$$ER = (C_D - C_U) \pi \sigma_v \sigma_z U$$

Where:  $ER \equiv Emission Rate (ng/sec);$ 

 $C_D \equiv \text{downwind concentration (ng/m}^3);$ 

 $C_U \equiv \text{upwind concentration (ng/m}^3);$ 

 $\pi \equiv 3.141....;$ 

 $\sigma_y \& \sigma_z \equiv$  horizontal and vertical dispersion coefficients (meters); and

 $U \equiv \text{mean wind speed (m/sec)}$ 

Some peculiarities are associated with the application of this equation. Low ambient concentrations can lead to both theoretically negative and unrealistically high emission rates. The former case develops when a downwind site has a concentration lower than the background site, while the latter case can result when a distant site is slightly higher than the background concentration. These difficulties have been resolved by ignoring all ambient concentrations less than 0.5 ng/m³ (except for the background concentration used as the upwind value).

This method of estimating emissions is most reliable over short time frames (hourly averages or less), rather than more extended sampling periods because of the way meteorological parameters are incorporated. Dispersion rates are greatly affected by sunlight induced thermal gradients, with four standardized conditions representing maximum dispersal rates (high sunlight) to minimum dispersal (overcast or at night).

In addition to the effect of thermal gradients, wind direction can vary significantly throughout a day. Because each sample was collected over the course of 24 to 72 hours, a wide range of potential conditions exist. Separate calculations using both maximum and minimum dispersion rates were made to provide the largest range possible. The maximum dispersion rate corresponds to bright sunlight during the entire sampling period, while the minimum rate assumes total overcast or night. Sites which were

nominally upwind of the mean wind direction were included in the calculations to cover variability in meteorological conditions.

An additional source of variability requiring simplifying assumptions is the distance and heading from the source to the sampling platforms. The approach adopted to counter this difficulty is to perform two sets of calculations, one assuming the Settling Basins are the primary source which incorporates the distance and heading from site FR01, and the other assuming the Filter Press is the primary source incorporating the distance and heading from site FR02.

All results obtained within  $\pm 45^{\circ}$  of the average wind direction were combined and compared with results obtained between  $\pm 45^{\circ}$  and  $\pm 90^{\circ}$ . Additionally, all results within  $\pm 90^{\circ}$  of the average wind direction were compared with the results obtained from sites greater than  $90^{\circ}$ . The purpose of these comparisons was to see if there were differences between emission rates calculated at the upwind and downwind sites.

Calculated emission rates are documented in table EC-1 below. All average, maximum and minimum values are in pounds PCB emitted per day. The number of results less than 0.01 lbs/day, between 0.01 and 0.1 lbs/day, and greater than 0.1 lbs/day, as well as the total number in each series of determinations is included in the table to provide a sense of the distribution of the values. Note that the upwind (between 90 and 180 degrees of the prevailing wind direction) emission rates calculated from FR01 are higher than the downwind values. This is a result of high concentrations observed around the filter press when it was upwind of the settling basins. With the exception of this case, the results obtained within  $\pm 45^{\circ}$  downwind generally indicate higher emission levels, as is expected for this type of determination.

**Table EC-1: Emission Rate Calculations from Ambient Results (lbs/day)** 

Calculations Based on the	Within 45 degrees   Between 45 and 90   Between 90 and					90 and 180
Filter Press as Sole Source			Maximum	_	Maximum	Minimum
Average	0.118	0.022	0.086	0.018	0.070	0.015
Max	0.410	0.061	0.363	0.053	0.342	0.088
Min	0.001	0.0002	0.0002	0.0001	0.00004	0.00001
# <0.01 lbs/day	2	13	3	8	8	12
# <0.1 lbs/day	23	27	12	13	5	8
# >0.1 lbs/day	15	0	6	0	7	0
Count	40	40	21	21	20	20
Settling Basins as Source	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum
Average	0.110	0.020	0.052	0.010	0.125	0.030
Max	0.457	0.061	0.429	0.057	0.751	0.194
Min	0.011	0.003	0.00010	0.00003	0.0001	0.00003
# <0.01 lbs/day	0	14	6	18	9	11
# <0.1 lbs/day	20	19	14	5	8	12
# >0.1 lbs/day	13	0	3	0	8	2
Count	33	33	23	23	25	25

The maximum and minimum values in this table represent unrealistic extreme values (up to 72 hours of direct sunlight or total darkness). Further incorporation of these results is based upon averaging the maximum and minimum dispersion conditions. All resulting averages are presented in table EC-2 below. Note that averaging all calculated values yields consistent rates between the different source scenarios.

Table EC-2: Average Calculated Emission Rates (lbs/day)

Averages	Filter Press	Settling Basin
Less than 45 Degrees	0.070	0.065
Between 45 and 90	0.052	0.031
Greater than 90	0.042	0.077
All Values	0.058	0.059
Project Average	0.059	

The project average of 0.059 lbs/day yields a theoretical total PCB loss of about 6.3 pounds during the 107 days of dredging. Process data provided by Montgomery Watson indicates that a total of 1326 pounds were removed. The potential loss to the atmosphere calculated in this way is 0.5% of the amount removed.

#### **Comparison With Emission Modeling**

Emission modeling was conducted both prior to and following the dredging project. In both instances, the Industrial Source Complex Short Term model (ISCST3) was employed. This is the regulatory model used in all stationary source modeling in Wisconsin. Within the model, five years of preprocessed National Weather Service data collected in Green Bay during 1983-1987 were used.

Modeling conducted prior to the project evaluated annual average concentrations derived from a single point source 30 feet square for simplicity's sake. Contour maps were prepared from which project design parameters were determined. A total of 1680 grid points were incorporated into the evaluation. Concentrations within each of the grid points was determined for a series of emission rates, ranging from 0.001 to 1.0 pounds PCB per day.

Direct comparison of this modeling effort with the observed results is complicated by a number of factors, including the tendency for ambient concentrations collected on a short term basis to be higher than estimated annual averages, in addition to the simplifying assumptions built into the model. The approach adopted for this comparison involved evaluating what percentage of the grid points within a 1 kilometer radius of the source are distinguishable from the urban background concentration, and comparing this with the percentage of monitoring sites within this radius above the same level.

When the data is viewed in this manner, it is seen that 100% of the grid points within 1 kilometer are distinguishable from urban background at all emission rates greater than 0.2 pounds per day. At 0.1 pounds per day, 94.0% are distinguishable, while this drops to

72.1% and 28.5% at 0.05 and 0.01 pounds per day, respectively. Monitoring results indicate that 90% of the monitoring sites within 1 kilometer are distinguishable during the 24 hour sampling, with 80% distinguishable during the 72 hour sampling.

Based on this evaluation, it appears that emission rates are likely to be between 0.05 and 0.1 pounds per day, which agrees with the calculations performed in the previous section. The various uncertainties involved in the comparing modeling to monitoring results make a more precise determination meaningless. During the course of the project, a total of 1326 pounds PCBs are estimated to have been removed. At a rate of 0.1 lb/day, a total of 10.7 pounds would have been lost to the atmosphere during the remediation. This corresponds to a loss of 0.8% of the total removed.

The second series of emission modeling incorporated several additional assumptions intended to improve the comparability of the data to the ambient results observed during monitoring. During the initial modeling, a single source was assumed for the sake of simplicity and because the remediation process was not well enough known by Air Management personnel to make more informed assumptions.

The second series of modeling calculations incorporated a more realistic scenario of multiple sources. Dimensions of the various potential sources were determined from a high resolution aerial photograph of the remediation area. Sources include the two settling basins, the filter presses, and the de-watered sediment pile. In addition, the loading of the de-watered sediment into trucks for removal to the landfill entails a source incorporated into the modeling effort. Receptors for the model were aligned with the actual monitoring stations, in an effort to model observed concentrations directly.

While a more accurate depiction of the physical layout of the sources was possible following the project, the relative contribution of each to and magnitude of total emissions remains unknown. As such, several different schemes were evaluated, each totaling emissions of 1 pound per hour. While this rate is significantly higher than the likely emission rate, results for other rates can be directly determined from this set of values.

A total of three different analyses were performed, two based on volatilization, and the third on particulate suspension. The first assumed that 75% of emissions derived from the settling basins, while 25% of the emissions were derived from the presses. These ratios were reversed for the second run, while the third run was based on particulate losses from the de-watered sediment pile, with 25% of the losses coming directly from the pile, and 75% from the loading operation.

Rather than determining an annual average concentration at evenly distributed receptor points as in the former analysis, theoretical maximum and second maximum daily values at the actual monitoring sites were determined using autumn meteorological data from each of the five years separately. These ten resulting values were then averaged for comparison with the monitoring data.

It should be noted that in spite of the greater accuracy in dimensions and locations of receptors and sources, these modeling assumptions are very approximate and unlikely to accurately reflect actual conditions. PCB loss to the atmosphere is a complex process with multiple pathways, including direct volatilization and suspension of particle bound material. The different scenarios were included to give an idea of what might be the dominant pathway of loss.

The following tables include the averaged model concentrations at each site for emission rates ranging from 0.005 to 1.0 lb/day, as well as the maximum observed concentrations during the course of monitoring. While all sites were included in the initial analysis, only sites through FR12 are reported here, as after that point monitoring results are difficult to distinguish from background. It should be noted that weather conditions will tend to prevent all of the sites from approaching their maximum potential values.

Table EC-3: 5 Year Average High and Second High Concentrations, ng/m<sup>3</sup>

Modeling 75% Basin, 25% Filter Press						Monitoring
Site	1.0 Lb/Day	0.1 Lb/Day	0.05 Lb/Day	0.01 Lb/Day	0.005 Lb/Day	Maximum
FR01	5127.2	512.7	256.4	51.3	25.6	28.5
FR02	948.8	94.9	47.4	9.5	4.7	79.7
FR03	399.0	39.9	19.9	4.0	2.0	3.8
FR04	2724.7	272.5	136.2	27.2	13.6	6.5
FR05	415.0	41.5	20.8	4.2	2.1	1.3
FR06	167.9	16.8	8.4	1.7	0.8	0.7
FR07	118.4	11.8	5.9	1.2	0.6	2.5
FR08	96.1	9.6	4.8	1.0	0.5	1.9
FR09	510.6	51.1	25.5	5.1	2.6	2.5
FR10	59.8	6.0	3.0	0.6	0.3	2.2
FR11	91.5	9.1	4.6	0.9	0.5	1.7
FR12	63.1	6.3	3.2	0.6	0.3	1.0

Table EC-4: 5 Year Average High and Second High Concentrations, ng/m<sup>3</sup>

Modeling, 25% Settling Basins, 75% Filter Press						Monitoring
Site	1.0 Lb/Day	0.1 Lb/Day	0.05 Lb/Day	0.01 Lb/Day	0.005 Lb/Day	Maximum
FR01	1827.4	182.7	91.4	18.3	9.1	28.5
FR02	2803.6	280.4	140.2	28.0	14.0	79.7
FR03	282.9	28.3	14.1	2.8	1.4	3.8
FR04	1228.0	122.8	61.4	12.3	6.1	6.5
FR05	596.7	59.7	29.8	6.0	3.0	1.3
FR06	232.3	23.2	11.6	2.3	1.2	0.7
FR07	109.4	10.9	5.5	1.1	0.5	2.5
FR08	86.3	8.6	4.3	0.9	0.4	1.9
FR09	1306.5	130.6	65.3	13.1	6.5	
FR10	100.1	10.0	5.0	1.0	0.5	2.2
FR11	66.4	6.6	3.3	0.7	0.3	1.7
FR12	59.7	6.0	3.0	0.6	0.3	1.0

Table EC-5: 5 Year Average High and Second High Concentrations, ng/m<sup>3</sup>

Modeling 25% Dust from Pile, 75% Loading					Monitoring	
Site	1.0 Lb/Day	0.1 Lb/Day	0.05 Lb/Day	0.01 Lb/Day	0.005 Lb/Day	Maximum
FR01	946.0	94.6	47.3	9.5	4.7	28.5
FR02	3864.1	386.4	193.2	38.6	19.3	79.7
FR03	451.5	45.2	22.6	4.5	2.3	3.8
FR04	284.1	28.4	14.2	2.8	1.4	6.5
FR05	534.9	53.5	26.7	5.3	2.7	1.3
FR06	299.9	30.0	15.0	3.0	1.5	0.7
FR07	109.9	11.0	5.5	1.1	0.5	2.5
FR08	80.8	8.1	4.0	0.8	0.4	1.9
FR09	1021.0	102.1	51.0	10.2	5.1	2.5
FR10	142.1	14.2	7.1	1.4	0.7	2.2
FR11	70.2	7.0	3.5	0.7	0.4	1.7
FR12	58.5	5.8	2.9	0.6	0.3	1.0

Evaluation of the different scenarios is based on comparing the relative concentrations observed at each site with those from the different models. While no single option explored above truly matches the monitoring data, it appears that the ratios associated with the particulate scenario (Table EC-5) are closest, which would imply that this may be the dominant route of PCB loss to the atmosphere associated with the remediation process. If this is the case, erection of a temporary structure within which to house the filter presses, sediment piles and loading operation could significantly reduce losses.

Evaluation of the magnitude of loss within the context of the second modeling effort indicates the emission rate may be between 0.01 and 0.05 lbs/day. Over the course of dredging, this would lead to a potential loss of between 1.0 and 5.5 pounds, or between 0.1 and 0.4% of the estimated total PCB removed.

All three attempts to estimate the emission rates yield consistent, low results, ranging from 0.01 to 0.1 pounds PCB per day lost. Assuming the average emission rate remained constant throughout the course of the project, this indicates a potential loss of up to 10.7 pounds, or 0.8% of the 1326 pounds of PCB removed from the river.